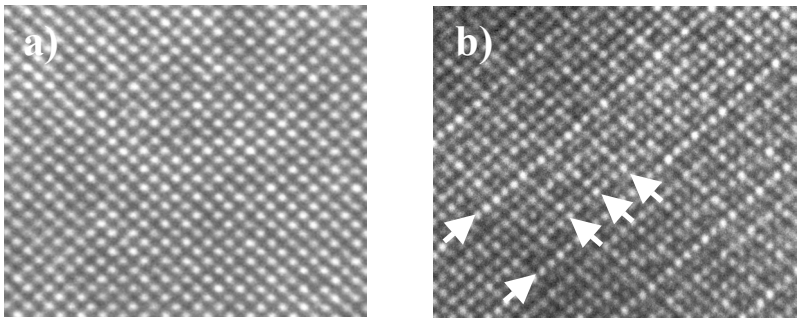
The Order-Disorder Transition in Bi_2O_3-Nb_2O_5 Fluorite-Like Dielectrics

M. Valant, B. Jancar, U. Pirnat, D. Suvorov
Advanced Materials Department, Jozef Stefan Institute, Ljubljana, Slovenia

The sintering behavior, the thermo-mechanical properties and the chemical compatibility of cubic Bi_2O_3-Nb_2O_5 fluorite-like solid solution (δ-BN_{SS}) with silver suggests the possible use of these materials in LTCC (low-temperature co-fired ceramic) technology. Because of the complexity of co-firing technology, the ceramic materials involved must be well understood in terms of their chemical and physical characteristics. The synthesis, sintering and dielectric properties of the cubic δ-BN_{SS} in the microwave frequency and radio-frequency ranges were already analyzed.[i] The permittivity as well as the dielectric losses measured in the MW frequency range increased with Nb_2O_5 concentration. The temperature coefficient of resonant frequency was found to be highly negative. In the same study a tetragonal Bi_3NbO_7, the so-called Type III, was synthesized in the temperature range from 850 to 880°C. We prepared dense, single-phase Type-III ceramics with 25 mol % of Nb_2O_5 and characterized their dielectric properties. The high permittivity in combination with modest dielectric losses and a low sintering temperature makes this material a candidate LTCC material. For this reason and because of the unusual phase-transformation sequence we engaged in a more detailed investigation of the synthesis and stability of this phase. We determined the temperature stability of the cubic and tetragonal phases for a composition with 25 mol % of Nb_2O_5 and characterized the influence of the phase transformation on the dielectric properties of the δ-BN_{SS}.



HRTEM images of the sample with 25mol% of Nb_2O_5 a) cubic phase and b) ordered tetragonal phase

We have shown that the incommensurate phase undergoes an order-disorder phase transition into a commensurately modulated crystal structure (Type III) at temperatures below 900°C. Studies of the influence of the superstructural ordering showed that in the tetragonal modification the dielectric losses are reduced due to a higher level of ordering, and the temperature coefficient of the resonant frequency gains a positive value, most probably due to the modifications in the oxygen sublattice. The investigations showed that the tetragonal modification exhibits good dielectric properties and that it is stable and can be sintered in a temperature range below 900°C, which is in accordance with the requirements for LTCC modules. This means that the tetragonal phase represents an interesting candidate for high-permittivity glass-free LTCC dielectrics.

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[i] Valant, M. & Suvorov, D., Dielectric Properties of the Fluorit-like Bi_2O_3-Nb_2O_5 Solid Solution and the Tetragonal Bi_3NbO_7. *J. American Ceramic Society*, 2003, **86** [6], 939–44.